Summary

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I

In this chapter the salient features of the mesogens, their classifications and structures have been delineated. The classifications of mesophases exhibited by thermotropic mesogens have also been described. A brief discussion on the known chemistry of mesogenic aryl azene oxides has been made. The purpose of the present investigation is cast against this background.

II

The experimental techniques used in this work for the detection and characterizations of the various mesophases are optical microscopy, differential scanning calorimetry and small angle X-ray diffraction methods. A brief discussion on the working principles of those methods along with their merits and limitations has been done in this chapter.

III

A convenient method for the synthesis of bis(*n*-alkyloxyarene)diazene-1-oxides has been developed. The family of bis[4-(*n*-alkyloxyphenyl)]diazene oxides, (RO-C_6H_4-N(O)=N-C_6H_4-OR), [R = *n*-alkyl group; CH_3 to $C_{14}H_{29}$] have been synthesized by zinc-ammonium chloride reduction of 4-(*n*-alkyloxy)nitro benzene in aqueous ethanol medium in a single step. The new synthetic method is economical, rapid

and environment-friendly. The synthesis, characterization, structure and mesogenic properties of hitherto unknown members ($R = C_{13}H_{27}$ & $C_{14}H_{29}$) of this series have been studied. Both the compounds exhibit smectic C phase. Polymorphism in solid state is shown by the compound ($R = C_{13}H_{27}$). The mesostructures were further confirmed by the small angle X-ray diffraction method. The molecular structures in solid state of two members ($R = C_8H_{17}$) & ($R = C_{14}H_{29}$) of this family have been determined by single crystal X-ray diffraction method. In the solid state at 293 K, the compound ($R = C_8H_{17}$) shows supramolecular aggregation of the molecules by weak C-H...O and C-H...π interactions. The layer formation in the solid state is detected and it appears to be the precursor of smectic C phase, obtained on melting. The molecular structure of the compound ($R = C_{14}H_{29}$) was determined by single crystal X-ray diffraction method at 150 K. It also shows layer formation in the solid state.

IV

A new series of bis[4-(*n*-alkyloxybenzoyloxy)phenyl]diazene oxides, ($RO\text{-}C_6H_4\text{-}C(O)O\text{-}C_6H_4\text{-}N(O)=N\text{-}C_6H_4\text{-}OC(O)C_6H_4\text{-}OR$), [R = n-alkyl group; CH_3 to $C_{14}H_{29}$] have been synthesized by zinc-ammonium chloride reduction of 4-(*n*-alkyloxybenzoyloxy)-4′-nitrobenzene in aqueous ethanol medium. Here the synthesis is chemoselective. The compounds have been characterized on the basis of spectral (IR, ^1H NMR, UV-VIS and FAB-MS) data. All the members of this family show thermotropic mesogenic behaviour over a good temperature range. The temperature range of the mesophases for bis-[4-(*n*-alkyloxybenzoyloxy)phenyl]diazene oxide is enhanced in comparison with that of the corresponding member of bis-[4-(*n*-alkyloxyphenyl)]diazene oxides. The compounds ($R = C_2H_5$ to C_7H_{15}) of this new

series show only nematic phase on melting up to the clearing point and also on reverse cooling below the isotropic temperature, whereas the compounds (R = C_9H_{19} to $C_{13}H_{27}$) exhibit smectic phase on melting followed by nematic phase which on cooling below the isotropic temperature re-enters to the smectic phase. The behaviour of compound (R = CH_3) is similar to that of compounds (R = C_9H_{19} to $C_{13}H_{27}$). Compound (R = C_8H_{17}) melts to nematic phase on heating, but on reverse cooling below the isotropic temperature the compound enters to the smectic phase first and then solidifies on further cooling. Compound (R = $C_{14}H_{29}$) shows only smectic phase. Majority of the members of this series show polymorphism in solid state. The solid-to-solid phase transitions were detected by DSC. Two members (R = $C_{12}H_{25}$ & $C_{14}H_{29}$) of this series show two solid-to-solid transitions during each cycle of heating and cooling. The structural identification of the mesophases has been done by small angle X-ray diffraction. The molecular structure of the compounds in solid state has been determined by single crystal X-ray crystallography. The molecules are stacked one over the other by C(aryl)–H···π(arene) interactions.

V

In this chapter we have undertaken a scheme to incorporate mesogenic behaviour in 1-phenyl-3-phenyltriazene-1-oxide systems. The design and synthesis of a new group of triazene-1-oxides, C_6H_5-N(O)=N-NH-C_6H_4-C(O)-O-C_6H_4-CH=N-C_6H_4-OR, [R = *n*-alkyl group; CH_3 to $C_{14}H_{29}$], have been made. The compounds have been characterized by spectroscopic techniques. Elemental analysis data of all the compounds confirm their proposed formulations. This family of four phenyl ring compounds linked by one triazene-1-oxide, one-ester and one-aldimine groups with a

terminal *n*-alkyloxy group uniformly show thermotropic mesogenic behaviour. Here, the length of the alkyloxy chain influences the mesogenic behaviour of the members. The compounds (R = CH_3 to C_6H_{13}) of this new series show nematic phase on melting up to clearing point. The compounds (R = C_7H_{15} to C_9H_{19}) exhibit smectic phase on melting followed by nematic phase. Compounds (R = $C_{10}H_{21}$ to $C_{14}H_{29}$) exhibit only smectic phase on melting.

VI

The synthesis of another new group of triazene-1-oxides, C_6H_5-N(O)=N-NH-C_6H_4-C(O)-O-C_6H_4-O-(O)C-C_6H_4-OR, [R = *n*-alkyl group; CH_3 to $C_{14}H_{29}$], have been made. The compounds have been characterized by spectroscopic techniques. All the members of this new family show thermotropic mesogenic behaviour. The replacement of aldimine group, present in the previously mentioned triazene-1-oxides series (chapter V), by ester group has remarkable effects on the mesogenic properties viz. lowering of the melting temperature (solid → mesophase) and enhancement of the temperature range for mesophases of the corresponding members. The compounds (R = CH_3 to C_8H_{17}) of this new homologous series show nematic phase on melting up to clearing point, whereas the compounds (R = C_9H_{19} to $C_{14}H_{29}$) exhibit smectic phase on melting followed by nematic phase. The effect of odd-even relationship on the melting temperature, clearing temperature (N→I) and phase entering temperature (I→N) is observed for this homologous series except the member (R = C_9H_{19}). The molecular structure of compound (R = C_9H_{19}) in solid state has been determined by single crystal X-ray diffraction method. Intermolecular hydrogen

bonding involving both N-H and C-H with oxygen atom of triazene-1-oxide is observed. There are N-H...O and C-H...O interactions. Dimer formation in solid state is also observed. The intermolecular C-H...π interactions are also detected. The intermolecular hydrogen bonding and intermolecular C-H...π interactions arrange the phenyl triazene-1-oxide fragments of the molecules in layer fashion within the molecular assembly. The single crystal X-ray analysis has also been done for the compound (R = $C_{11}H_{23}$) and its data collection was made at 150 K.